QUANTITATIVE DECONVOLUTION OF ^{13}C NMR SPECTRA OF ILLINOIS #6 COAL

M.A. Jacintha,[a] C.R. Dybowski,[a] W.H. Calkins,[b] W.D. Provine,[b] M.T. Klein[b]
Center for Catalytic Science and Technology
[a]Department of Chemistry and Biochemistry
and
[b]Department of Chemical Engineering
University of Delaware
Newark, DE 19716

INTRODUCTION

The quantification of chemical functionality is necessary to construct a picture of the structure of coal. The aromaticity of coal has been determined in a relatively quantitative manner using solid-state ^{13}C NMR spectroscopy,[1] although there has been a great deal of discussion about how this process can be carried out.[2] In this study, we discuss how one might further deconvolute the carbon spectrum of coal, into various aromatic and aliphatic components.

EXPERIMENTAL

Illinois #6 coal was obtained from the Argonne Premium Coal Sample Bank. The solid coal was analyzed by variable-contact-time solid-state ^{13}C CPMAS NMR spectroscopy, with a Chemagnetics m100S spectrometer operating at 25.1 MHz for carbon. Samples were kept in Kel-F^R spinners to avoid spurious resonances from spinner material. Typical spinning speeds were 3 kHz. The acquisition time was 50 ms with a ^{1}H 90° pulse width of 6.5 μs and a pulse delay of 1 s. Quantification of both the original and the deconvoluted spectra were performed by fitting the integral intensities to the magnetization-recovery equation.[3] The CPMAS spectra obtained at the various contact times were digitized using a TANDY Digitizer Pad, corrected for baseline roll and analyzed with the Peakfit^R computer fitting program.

RESULTS

Various combinations of functions were tried. Of the many sets tried, only the combination of Lorentzian and Voigt functions given in Tables 1 and 2 fit the CPMAS spectra

obtained at various contact times <u>over the full range of contact times</u>. The aromatic region was resolved into three Lorentzians and one Voigt function. Similarly, the aliphatic region was resolved into two Lorentzians and two Voigts. The chemical-shift range, type of line-shape function, $T_{1\rho H}$, T_{CP} and 'f' for each of the aromatic and aliphatic components are listed in Tables 1 and 2, respectively.

From the data in Tables 1 and 2, one sees that the parameters determining the cross-polarization behavior of the various components vary by up to a factor of 4 for $T_{1\rho H}$, and by a factor of 15 for T_{CP}. With such a wide variation of the values of the parameters for various components of the coal, it is readily understandable why integration of a CP-MAS spectrum taken at a single contact time cannot properly represent the distribution of carbon as accurately as possible. These results are related to the usual time constants determined for the aromatic and aliphatic regions, in that weighted averages of the $1/T_{1\rho H}$ and $1/T_{CP}$ of the components in a region are equal to those determined by variation of the integrals with contact time.[4]

In Figure 1, a simulated spectrum of this coal (based only on CPMAS-derived parameters) is compared with a fully relaxed Bloch-decay (BD) spectrum of the same coal. While the BD spectrum is relatively noisy, the simulated spectrum closely approximates its features. The BD spectrum was obtained with a pulse delay of 120 s. We have found that, to obtain fully relaxed spectra one must wait much longer than the suggested pulse delay of 20 s.[5]

One may be tempted to assign the components generated by this process, through comparison of the mean chemical shifts to those of pure model compounds. However, this is an oversimplification of the speciation. The range of shifts for each component as indicated by the half-width in the Tables is rather wide. In these ranges fall many different carbon functionalities. Thus, an analysis of this type will only coarsely describe the results. For example, the two downfield aromatic components <u>may</u> be associated with carbon-oxygen linkages. One possible solution to assigning the NMR components is correlation of these results with other measures of the coal structure (obtained by wet-chemical analysis or other spectroscopic investigation) using the techniques of factor analysis.[6] To do this requires the analysis of many different coal samples such as the Argonne Premium Coal Samples. We are exploring this possibility.

References
1.   Maciel, G.E.; Sindorf, D.W. *J. Am. Chem. Soc.* **1980**, *102*, 7607.

2.   Snape, C.E.; Axelson, D.E.; Botto, R.E.; Delpuech, J.J.; Tekely, P.; Gerstein, B.C.; Pruski, M.; Maciel, G.E.; Wilson, M.A. *Fuel* **1989**, *68*, 547.

3.   Botto, R.E.; Winans, R.E. *Energy and Fuels* **1987**, *1*, 173.

4.   Solum, M.; Pugmire, R. J.; Grant, D. M. *Energy and Fuel* **1989**, *3*, 187.

5.   Snape, C.E.; Love, G.D. *Prepr. of the Fuel Chem. Div.* **1991**, *36*, 877.

6.   Malinowski, E.F.; Howery, D.F. *Factor Analysis in Chemistry*; Wiley: New York, 1980.

Table 1. Aromatic Components of Argonne Illinois #6 Coal

$<\delta>$ (ppm)	Function	$T_{1\rho H}$ (ms)	T_{CP} (ms)	f
170 ± 5	Lorentzian	1.7 ± 0.05	0.39 ± 0.004	0.14 ± 0.02
160 ± 7.5	Lorentzian	3.0 ± 0.05	0.43 ± 0.004	0.16 ± 0.02
150 ± 12	Voigt	6.0 ± 0.05	0.30 ± 0.004	0.27 ± 0.02
125 ± 5	Lorentzian	3.5 ± 0.05	0.13 ± 0.004	0.12 ± 0.02

Table 2. Aliphatic Components of Argonne Illinois #6 Coal

$<\delta>$ (ppm)	Function	$T_{1\rho H}$ (ms)	T_{CP} (ms)	f
75 ± 5	Lorentzian	4.0 ± 0.05	0.05 ± 0.004	0.07 ± 0.02
65 ± 7.5	Voigt	3.8 ± 0.05	0.18 ± 0.004	0.12 ± 0.02
50 ± 7.5	Lorentzian	7.0 ± 0.05	0.14 ± 0.004	0.09 ± 0.02
25 ± 2	Voigt	1.0 ± 0.05	0.75 ± 0.004	0.04 ± 0.02

Figure 1. Comparison between a simulated fully-relaxed spectrum
and a Bloch-decay spectrum